

AD-A132 830

A GENERAL SYNTHESIS FOR DITUNGSTEN TETRACARBOXYLATES
PREPARATION OF W-W Q. (U) INDIANA UNIV AT BLOOMINGTON
DEPT OF CHEMISTRY M H CHISHOLM ET AL. 08 SEP 83

1/1

UNCLASSIFIED

INDU/DC/TR-83/4-MC N00014-79-C-0044

F/G 7/2

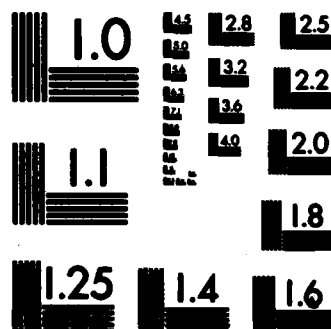
NL



END

FORMED

1983



MICROCOPY RESOLUTION TEST CHART
NATIONAL BUREAU OF STANDARDS-1963-A

OFFICE OF NAVAL RESEARCH

Contract No. N00014-79-C-0044

Task No. NR 056-703

TECHNICAL REPORT NO. INDU/DC/TR-83/4-MC

A GENERAL SYNTHESIS FOR DITUNGSTEN TETRACARBOXYLATES.
PREPARATION OF W-W QUADRUPLE BONDS BY REDUCTIVE-ELIMINATION
(ALKYL GROUP DISPROPORTIONATION) FROM 1,2-DIETHYL COMPOUNDS
WITH W-W TRIPLE BONDS.

by

M.H. Chisholm, H.T. Chiu and J.C. Huffman

Prepared for Publication

in

Journal of the American Chemical Society

Department of Chemistry
Indiana University
Bloomington, IN 47405

September 8, 1983

DTIC
SELECTE
SEP 23 1983
A

Reproduction in whole or in part is permitted for
any purpose of the United States Government.

This document has been approved for public release
and sale; its distribution is unlimited.

88 09 19 076

DTIC FILE COPY

AD-A 132 830

REPORT DOCUMENTATION PAGE		READ INSTRUCTIONS BEFORE COMPLETING FORM
1. REPORT NUMBER INDU/DC/TR-83/4-MC	2. GOVT ACCESSION NO. AD-A132 830	3. RECIPIENT'S CATALOG NUMBER
4. TITLE (and Subtitle) A General Synthesis for Tungsten Tetracarboxylates. Preparation of W-W Quadruple Bonds by Reductive-Elimination (Alkyl Group Disproportionation) from 1,2-Diethyl Compounds with W-W Triple Bonds		5. TYPE OF REPORT & PERIOD COVERED Technical Report 1983
7. AUTHOR(s) M.H. Chisholm, H.T. Chiu and J.C. Huffman		6. PERFORMING ORG. REPORT NUMBER INDU/DC/TR-83/4-MC
8. PERFORMING ORGANIZATION NAME AND ADDRESS Department of Chemistry Indiana University Bloomington, IN 47405		9. CONTRACT OR GRANT NUMBER(s) N00014-79-C-0044
11. CONTROLLING OFFICE NAME AND ADDRESS Office of Naval Research Department of the Navy Arlington, VA 22217		10. PROGRAM ELEMENT, PROJECT, TASK AREA & WORK UNIT NUMBERS
14. MONITORING AGENCY NAME & ADDRESS (if different from Controlling Office)		12. REPORT DATE September 8, 1983
		13. NUMBER OF PAGES 8
		15. SECURITY CLASS. (of this report)
		15a. DECLASSIFICATION/DOWNGRADING SCHEDULE
16. DISTRIBUTION STATEMENT (of this Report) This document has been approved for public release and sale; its distribution is unlimited.		
17. DISTRIBUTION STATEMENT (of the abstract entered in Block 20, if different from Report)		
18. SUPPLEMENTARY NOTES		
19. KEY WORDS (Continue on reverse side if necessary and identify by block number) dinuclear reductive-elimination, tungsten, quadruple bonds, carboxylates		
20. ABSTRACT (Continue on reverse side if necessary and identify by block number) → A general high yield synthesis for $W_2(O_2CR)_4$ compounds is proposed based on eq. 1, wherein a W-W triple bond is converted to a quadruple bond, and this has been established for R = Me, Et and t-Bu. 1 $W_2Et_2(NMe_2)_4 + 4RCOOCOR \longrightarrow W_2(O_2CR)_4 + 4RCONMe_2 + C_2H_4 + C_2H_6$		

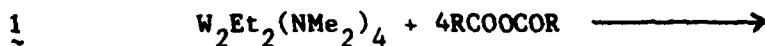
A General Synthesis for Ditungsten Tetracarboxylates.

Preparation of W-W Quadruple Bonds by Reductive-Elimination (Alkyl Group Disproportionation) from 1,2-Diethyl Compounds with W-W Triple Bonds.

The search for compounds containing W-W quadruple bonds, particularly ditungsten tetracarboxylates, is one of the fascinating stories in the development of the chemistry of compounds containing multiple bonds between metal atoms.^{1,2} At this time there are two reports of the preparation and characterization of $W_2(O_2CR)_4$ compounds. Sattelberger and McLaughlin³ reported in 1981 that reduction of $W_2Cl_6(THF)_4$ with 2 equivalents of sodium amalgam in THF at $-20^\circ C$, followed by addition of sodium trifluoroacetate (4 equiv) gave, upon work up, $W_2(O_2CCF_3)_4$ in 20% yield based on tungsten. More recently Cotton and Wang⁴ reported a higher yield synthesis (ca. 55% based on W) for the benzoate, $W_2(O_2CPh)_4 \cdot 2THF$, from Na/Hg reduction of WCl_4 in THF followed by treatment with sodium benzoate. We wish here to report a general high yield synthesis for $W_2(O_2CR)_4$ (MEM) compounds based on reductive elimination (alkyl group disproportionation) from $W \equiv W$ containing compounds.

Hydrocarbon solutions of $1,2-W_2Et_2(NMe_2)_4$ ⁵ react quickly at room temperature with acid anhydrides $RCOOCOR$, where $R = Me, Et$ and $t-Bu$, according to equation 1. These reactions appear quantitative when they are carried out in sealed nmr tubes and followed by 1H nmr spectroscopy. In the absence of oxygen donor solvents, the tetracarboxylates are isolated either as weakly ligated polymers $[W_2(O_2CR)_4]_n$, where $R = Me$ or Et ⁶, as shown in Figure 1, or as the $RCONMe_2$ adduct $W_2(O_2C-t-Bu)_4 \cdot 2t-BuCONMe_2$, by crystallization from benzene or hexane. These

new compounds are bright yellow, crystalline, volatile, air-sensitive compounds and appear analogous to the two previously reported related compounds. An extension of eq. 1 to include other R groups seems obvious.



The present finding is of interest and worthy of note because it reveals that by appropriate synthetic strategy W-W triple bonds can be converted to W-W quadruple bonds.⁷ This is the first observation of this transformation.



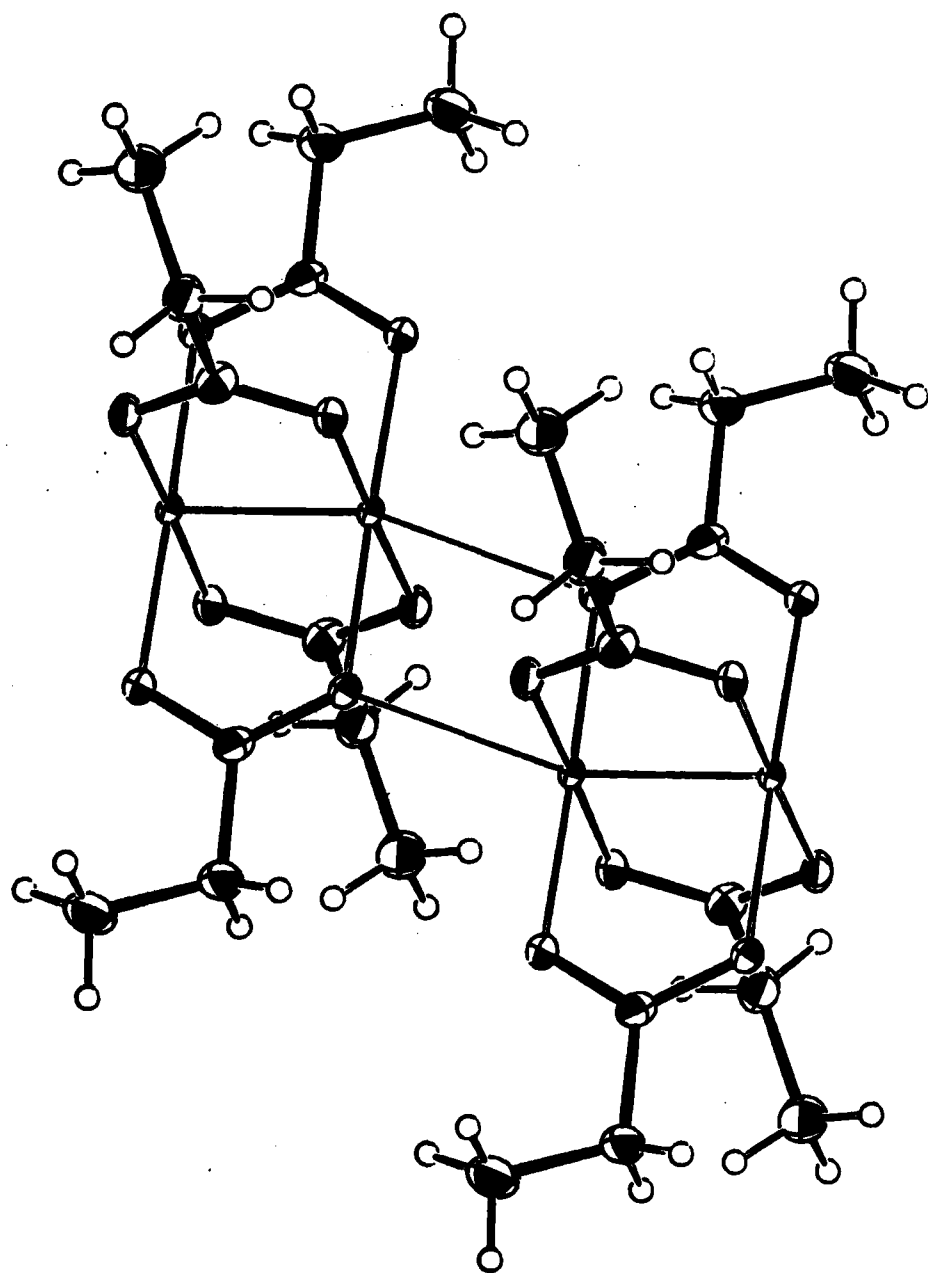
Accession For		
NTIS GRA&I	<input checked="" type="checkbox"/>	
DTIC TAB	<input checked="" type="checkbox"/>	
Unannounced	<input type="checkbox"/>	
Justification		
Distribution/		
Availability Codes		
Avail and/or		
at	Special	
A		

Acknowledgement We thank the Office of Naval Research and the Wrubel
Computing Center for support.

1. Cotton, F.A.; Walton, R.A. "Multiple Bonds Between Metal Atoms," John Wiley, 1982.
2. Cotton, F.A. Chem. Soc. Rev. 1983, 12, 35.
3. Sattleberger, A.P.; McLaughlin, K.W.; Huffman, J.C. J. Am. Chem. Soc. 1981, 103, 2880.
4. Cotton, F.A.; Wang, W. Inorg. Chem. 1982, 21, 3860.
5. Chisholm, M.H.; Haitko, D.A.; Huffman, J.C., J. Am. Chem. Soc., 1981, 103, 4046.
6. Crystal data for $W_2(O_2CET)_4$ at $-160^\circ C$: $a = 9.377(2)\text{\AA}$, $b = 8.271(2)\text{\AA}$, $c = 5.527(1)\text{\AA}$, $\alpha = 102.49^\circ$, $\beta = 84.61(1)^\circ$, $\gamma = 89.45(2)^\circ$, $Z = 1$, $d_{\text{calcd}} = 2.631\text{gcm}^{-3}$ and space group $P\bar{1}$. Data collection was performed using standard moving crystal-moving detector techniques (MoK α $6^\circ < 2\theta < 50^\circ$). Of 1477 unique intensities, 1464 having $F > 2.33\sigma$ (F) were used in the refinement. The W atom position was located in a Patterson and all remaining atoms, including H atoms, were located in the Fourier synthesis. A final difference Fourier was featureless, the largest peak being $0.83e/\text{\AA}^3$, located near the W position. Final residuals are $R(F) = 0.016$ and $R_w(F) = 0.015$.
7. Reactions between $W_2Et_2(NMe_2)_4$ and each of CO_2 and $ArNNNHAr$ do not appear to parallel reactions wherein Mo-Mo triple bonds are converted to Mo-Mo quadruple bonds. These reactions are under continuing investigation: Chetcuti, J.J.; Chisholm, M.H.; Folting, K., Haitko, D.A., Huffman, J.C. J. Am. Soc. 1982, 104, 2138.

Caption to Figure 1

An ORTEP view of the centrosymmetric $W_2(O_2C\text{Et})_4$ molecule showing the connectivity in the infinite chain $[W_2(O_2C\text{Et})_4]_n$. Pertinent distances (Å) and angles ($^\circ$) (averaged where appropriate), are W-W = 2.189(1), W-O = 2.08(2), W---O = 2.665(4), W-W-O = 91(1), W-W---O = 161.6(1). $^\circ$



END

FILMED

10-83

DTIC